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effluent discharge for discharging a wastewater stream as feed directly to the carbon bed and containing byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l. Support for the Amendment is found in original Claims 15 and 16.

New Claims 21 and 22 have been amended to more particularly point out and distinctly claim that which Applicants regard as their invention and to recite (Claim 21) organic chemical means for contacting said carbon bed product stream metal ions with dithiocarbamate to precipitate said copper ions for removing said copper ions from solution and (Claim 22) inorganic chemical means for contacting said carbon bed product stream metal ions with iron sulfate ( $FeSO_4$ ) or aluminum sulfate ( $Al_2(SO_4)_3$ ) or aluminum sulfate to co-precipitate said copper ions. No new matter has been added.

35 U.S.C. §112

Claims 12-19 stand rejected under 35 U.S.C. §112, second paragraph, as indefinite.

Claims 12-19 have been amended to recite the language and limitations as suggested by the Examiner in the Office Action.

It is believed that the amendments to the claims have corrected the indefiniteness, and the rejection of Claims 12-19

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under 35 U.S.C. §112, second paragraph, is respectfully requested to be withdrawn.

For the foregoing reasons, the rejection of Claims 12-19 is believed to have been overcome by the Amendments to the Claims, and the rejection is believed to have been overcome and is respectfully requested to be withdrawn.

35 U.S.C. §102

Claims 12-19 stand rejected under 35 U.S.C. §102(b) as anticipated by Busch et al. U.S. Patent No. 5,558,775 (hereinafter "Busch").

Busch discloses treating hazardous waste water having filter media and high filter rates wherein chemicals oxidize organic compounds and precipitate dissolved solids.

Applicants' Claims 12-19 require feeding a high solids (50 - 2000 mg/l) stream directly from a chemical mechanical polishing unit to and through a carbon bed to allow for removal of hydrogen peroxide from the stream. In Applicants' invention as claimed, the nature of the solids, along with the generation of gas during the peroxide decomposition, which helps "scrub" the column, allow the solids to pass through without plugging. Removal of hydrogen peroxide is necessary to reduce the cost of using dithiocarbamate. If the peroxide is not removed using carbon, the

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dithiocarbamate will react with it prior to reacting with the copper, resulting in excessively high chemical costs. Hydrogen peroxide also causes sludge generated in the precipitation step to float if it is not first decomposed.

Busch discloses the use of several filters to remove suspended solids prior to carbon filtration. In the Busch examples, solids are removed in the filtration units 50 and 52, both of which precede the carbon filter. The majority of the solids are removed prior to passing the waste water through the carbon bed 54. This is necessary to prevent plugging of the carbon filters. In the case of Busch, the carbon filters are design strictly for the removal of organic contaminants. In Applicants' invention as claimed, the carbon is used strictly for degradation of peroxide.

Busch at col. 3, line 44, describes a multimedia filter with a layer of anthracite. The purpose of this filter is strictly solids removal, with the anthracite being the primary filtration layer - not a carbon filter mechanism.

Busch, at col. 5, lines 9 - 63, describe the process of removing solids in the first set of filters 50, adding a precipitant from tank 90, removing the thus formed precipitate in the 2nd set of filters 52, then passing the stream with the solids removed through the carbon filters 54. Again, solids are removed prior to carbon filtration.

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Busch is significantly different from Applicants' invention as claimed. Busch uses a variety of filtration devices, multimedia filters, and carbon filters to remove suspended solids and organic materials ahead of downstream precipitation processes. Applicants' invention as claimed differs significantly in that Applicants do not remove suspended solids or organics ahead of Applicants' precipitation process for removing heavy metals.

Precipitation of heavy metals in Applicants' apparatus is accomplished by first removing excess oxidizer catalytically via carbon, followed by DTC/sulfide or iron or aluminum salts precipitation.

Applicants' apparatus invention as claimed has the distinct advantage of letting the solids (non-regulated solids) pass through the oxidant removal process, while the copper (a commonly regulated compound) is removed with significantly reduced chemical dosages since peroxide would interfere with the precipitants we are using. The chemical dosage required to treat the copper after the high levels of peroxide are removed is significantly lowered by reducing the peroxide to 1 ppm or less. DTC and sulfide react directly with the peroxide, being reduced by the peroxide. Aluminum and iron compounds cause catalytic decomposition of the peroxide forming hydroxyl radically which keep copper

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in the oxidized state while generating oxygen and hydrogen gas bubbles which interfere with the precipitated solids removal process. In Applicants' invention as claimed, chemical precipitation takes place after the carbon filter, not before as in Busch.

For the foregoing reasons, the rejection of Claims 12-19 under 35 U.S.C. §102 as anticipated by Busch et al. U.S. Patent No. 5,558,775 is based on an insufficient reference and is respectfully requested to be withdrawn.

35 U.S.C. §103

Claims 12-19 stand rejected under 35 U.S.C. §103(a) as unpatentable over Hagimori U.S. Patent No. 5,348,724 (hereinafter "Hagimori") in view of Bowers U.S. Patent No. 5,045,213 (hereinafter "Bowers").

Applicants' invention as claimed provides novel apparatus for the removal of copper ions including a chemical mechanical polishing unit for chemical mechanical polishing integrated circuits, the chemical mechanical polishing unit having a chemical mechanical polishing effluent discharge for discharging a wastewater stream containing byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l and

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passing a wastewater solution containing copper ions first directly through a carbon adsorption column, without prior micro-filtration or ultra-filtration removal of silica, alumina slurry solids, to remove catalytically the hydrogen peroxide ( $H_2O_2$ ) and then through means for contacting the wastewater solution containing copper ions to attach the copper, with an organic dithiocarbamate to precipitate the copper.

In one aspect, Applicants' invention as claimed provides novel apparatus for the removal of copper ions including passing a wastewater solution containing copper ions directly from a chemical mechanical polishing unit for chemical mechanical polishing integrated circuits, the chemical mechanical polishing unit having a chemical mechanical polishing effluent discharge for discharging a wastewater stream containing byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l first through a carbon adsorption column, preferably without prior micro-filtration/removal of silica, alumina slurry solids, to remove catalytically the hydrogen peroxide ( $H_2O_2$ ) and then through means for reacting the wastewater solution containing copper ions with an inorganic ferrous sulfate or aluminum sulfate to precipitate the copper.

Hagimori only discloses the decomposition of hydrogen peroxide using activated carbon and not metal removal. The difference is that Applicants' invention as claimed has a significant quantity of solids in the wastewater feed stream. Hagimori does not mention anything about solids. Hagimori is using solids-free solutions, or Hagimori is doing tests in beakers, instead of in columns, which plug when solids are present. In addition, Hagimori suggests peroxide decomposition be conducted at elevated temperatures (60°C). All Applicants' tests are conducted at ambient temperatures.

There is no motivation to combine the Hagimori and Bowers references. Bowers discloses waste water treatment for removing heavy metals optimized by removing and filtering a sample flow based on pH to precipitate the metals.

Applicants' invention as claimed provides means for removing hydrogen peroxide with activated carbon (Claims 4-6). If the peroxide is not removed prior to treatment with dithiocarbamates, the dosages of dithiocarbamates will be prohibitively high. This is due to the reaction of the dithiocarbamates with hydrogen peroxide as discussed above.

Hagimori discloses decomposing hydrogen peroxide and recycling hydrogen peroxide containing sulfuric acid. Hagimori uses

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from a wastewater from a byproduct polishing slurry from the chemical mechanical polishing (CMP) of integrated circuit microchips to precipitate the metal ions and form an environmentally clean water discharge product.

Applicants' invention as claimed provides apparatus which passes the solids-containing waste slurry without appreciable retention in the column and removes peroxide and copper occurring with the passage of solids (50 to > 2000 mg/l). A high solids feed is passed through packed columns without the solids impacting the performance of that column. This is not intuitively obvious and has not been for many years. Further evidence of the non-obviousness of Applicants' invention as claimed is observed in the chemical mechanical polishing CMP wastewater slurry is opaque, not transmitting to light, and infinitely outside the range of these feed specifications. Subsequent work in the field has been run with feeds having suspended solids in excess of 20% by weight (i.e. 200,000 mg/l).

Hagimori addresses the historic destruction of peroxide with activated carbon. However, Hagimori is using 10 mm "rocks" and processes a feed stream through this media. Only once does Hagimoro address the use of activated carbon (which is 34um in diameter) but utilizes "clean" particle free acid and peroxide

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the historic destruction of peroxide with activated carbon. However, Hagimori uses 10 mm "rocks" and processes a feed stream through this media. Only once does Hagimori address the use of activated carbon (which is 34  $\mu\text{m}$  in diameter) but utilizes "clean" particle free acid and peroxide introduced in a stirred beaker where no particles would be present. In actuality, the activated carbon slurry would readily pass through Hagimori's 10 mm column without being retained.

Applicants' invention as claimed does not emphasize the claim that carbon decomposes peroxide. Applicants' invention as claimed is based on the finding that Applicants are able to feed water with up to 2000+ mg/l of suspended solids material through the carbon column without plugging the column or removing any appreciable amount of suspended solids. This is counter-intuitive to what anyone versed in water treatment would expect. Removing the peroxide is necessary to obtain reasonable chemical precipitation consumption (peroxide is reduced by DTC/sulfides).

Bowers is precipitating metals after solids removal without removing peroxide where Applicants' invention as claimed is taking this same 2000+ mg/l suspended solids stream that passed through the carbon column without plugging and directly precipi-

tating the metals. Indeed in order for the Bower process to function, turbidity must be removed by filtration. In Applicants' invention as claimed, the turbidity of the 500 mg/l to 2000 mg/l solution is so high as to be not readable.

There is no motivation to combine the Hagimori and Bowers, references. Even assuming, but not granting or admitting that one would have combined the Hagimori and Bowers references, one would not have come up with Applicants' invention as claimed of novel apparatus for the removal of copper ions by passing a wastewater solution containing copper ions directly from a chemical mechanical polishing unit for chemical mechanical polishing integrated circuits, said chemical mechanical polishing unit having a chemical mechanical polishing effluent discharge for discharging a wastewater stream containing byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l first through a carbon adsorption column, preferably without prior micro-filtration or ultra-filtration - removal of silica, alumina slurry solids, to remove catalytically the hydrogen peroxide ( $H_2O_2$ ) and then providing a second step chemical precipitation unit operation for receiving a carbon bed product stream from the carbon adsorption bed and for removing the metal ions from solution, except on the basis of reconstruc-

tive hindsight after having had the benefit of Applicants' full disclosure as set forth in the detailed description of Applicants' Specification.

Applicants' invention as claimed provides means for removing metal ions from wastewater by providing a first step chemical mechanical polishing unit for chemical mechanical polishing integrated circuits, the chemical mechanical polishing unit having a chemical mechanical polishing effluent discharge for discharging a wastewater stream containing byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l connected directly to a carbon adsorption bed for receiving a wastewater feed containing metal ions in solution, wherein the wastewater feed contains solids sized in the range of about 0.01-1.0  $\mu\text{m}$  in an amount higher than about 50 mg/l, in combination with providing a second step chemical precipitation unit operation for receiving a carbon bed product stream from the carbon adsorption bed and for removing the metal ions from solution. Applicants' invention as claimed provides an apparatus which removes metal ions from wastewater containing solids in an amount higher than about 100 mg/l, preferably in an amount higher than about 500 mg/l, e.g., by way of example in an amount in the range of about 500-2000 mg/l.

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A wastewater feed containing hydrogen peroxide and metal ions in solution is connected directly to the carbon column to reduce the concentration of the hydrogen peroxide and form a carbon bed effluent having concentration levels of hydrogen peroxide less than about 1 mg/l (1 ppm). In one aspect, the metal ions are copper ions. In one aspect, the metal ions are copper ions at a concentration level in the range of about 1-100 mg/l.

The chemical precipitation unit operation includes means for contacting copper ions in the carbon bed product stream metal ions with an organic carbamate means to precipitate the copper ions. In one embodiment (Independent Claim 21), the organic carbamate means includes dithiocarbamate.

In an alternative embodiment (Independent Claim 22), the chemical precipitation unit operation includes means for contacting copper ions in the carbon bed product stream with an inorganic iron sulfate ( $FeSO_4$ ) or aluminum sulfate ( $Al_2(SO_4)_3$ ) to co-precipitate the copper ions at a neutral or elevated pH.

Applicants' invention as claimed provides means for removing metal ions from a wastewater from a byproduct polishing slurry. In one embodiment, Applicants' invention as claimed provides means for removing metal ions, e.g., such as copper metal ions,

introduced in a stirred beaker where no particles would be present. In actuality, the activated carbon slurry would readily pass through the Hagimori 10 mm column without being retained.

Bowers is significantly different from Applicants' invention as claimed. Bowers uses a variety of filtration devices, i.e., diatomaceous filters and/or pretreatment steps, i.e., alum/soda coagulation/flocculation followed by sand filtration to remove solids prior to carbon filtration. Applicants' invention as claimed differs significantly in that Applicants' invention does not remove suspended solids ahead of the carbon filter/chemical precipitation process for removing heavy metals. Applicants' invention as claimed has the distinct advantage in high solids loading applications such as this, of letting the solids which are largely non-regulated solids pass through the oxidant removal steps and through the chemical precipitation step. The copper, a commonly regulated metal, is removed in the chemical precipitation system, where it can be regenerated to form a concentrated copper solution that is recoverable by electrolytic recovery process or by specialized precipitation processes which precipitate the copper in a form suitable for resale. The copper-free solids then can be discharged to a sewer, if the suspended solids

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levels of this stream when combined with the remainder of the plant's effluent are below regulatory limits.

Alternately, the copper-free solids can be removed by coagulation and settling, direct filtration, and disposed of according to appropriate regulations.

Applicants' invention as claimed differs from Hagimori in that Applicants' invention provides a proper control of system chemistry to feed water with up to 2000+ mg/l of suspended solids material through a carbon column without plugging the column or removing any appreciable amounts of suspended solids. This is counter-intuitive to what anyone versed in the art of water treatment would expect. Additionally, removing the peroxide is necessary to obtain a reasonable life for the chemical precipitation resin. Peroxide in the presence of heavy metals, such as copper, can produce hydroxyl radicals (Fenton's Reageant) which degrade ion exchange resin polymers.

Applicants' invention as claimed provides novel apparatus for the removal of copper ions from a byproduct polishing slurry wastewater solution containing copper from the chemical mechanical polishing (CMP) of integrated circuits of semiconductor microelectronic chips. The chemical mechanical polishing (CMP) planarization process introduces copper into the process water,

and governmental regulations for the discharge of wastewater from the chemical mechanical polishing (CMP) planarization process are as stringent as the wastewater from an electroplating process, even though CMP planarization is not an electroplating process. The copper ions in solution in the wastewater must be removed from the byproduct polishing slurry for acceptable wastewater disposal. The chemical mechanical polishing planarization of the microchip produces a byproduct "grinding" (polishing) slurry wastewater which contains copper ions at a level of about 1-100 mg/l. The byproduct polishing slurry wastewater from the planarization of the microchip also contains solids sized at about 0.01-1.0  $\mu\text{m}$  at a level of about 500-2000 mg/l (500-2000 ppm). An oxidizer of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) typically is used to help dissolve the copper from the microchip. Accordingly, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) at a level of about 300 ppm and higher also is present in the byproduct polishing slurry wastewater. A chelating agent such as citric acid or ammonia also can be present in the byproduct polishing slurry to facilitate keeping the copper in solution. If hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is present, dithiocarbamate reacts with the hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) before the dithiocarbamate operates to pull the copper ions from the complexing agent. Accordingly, hydrogen peroxide present in the

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precipitating step makes it difficult to precipitate the copper, and a large amount of the dithiocarbamate organic precipitating solution is required to be used.

Applicants' apparatus as claimed overcomes all of these problems and removes the copper from the waste slurries near the point of generation and permit a copper-free waste to pass to discharge and neutralization. Applicants' apparatus as claimed overcome all of these problems and removes copper ions from solution for acceptable wastewater disposal of byproduct polishing slurries containing high amounts of suspended solids and removes the copper ions from solution containing high amounts of suspended solids efficiently and economically.

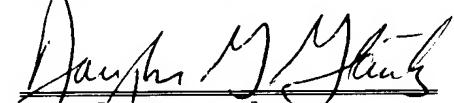
For the foregoing reasons, the rejection of Claims 12-19 under 35 U.S.C. §103(a) as unpatentable over Hagimori U.S. Patent No. 5,348,724 in view of Bowers U.S. Patent No. 5,045,213 is based on an improper combination of references and further is based on insufficient reference and is respectfully requested to be withdrawn.

Attached hereto is a marked-up version of the changes made to the Abstract by the current Amendment. The attached pages are captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE."

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Reconsideration of this application is requested.

Respectfully submitted,



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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE SPECIFICATION**

On page 1, on the first line after the title, insert:

--This patent application is a Division of prior, co-pending U.S. Patent Application Serial No. 09/113,981, filed July 10, 1998, now U.S. Patent No. 6,315,906.--.

12. (Amended) Apparatus for removing metal ions from wastewater, comprising:

(a) a chemical mechanical polishing unit for chemical mechanical polishing integrated circuits, said chemical mechanical polishing unit having a chemical mechanical polishing effluent discharge for discharging a wastewater feed containing byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l;

[(a)] (b) a carbon bed connected directly to said chemical mechanical polishing effluent discharge, said bed providing means for receiving [a] said wastewater feed containing [metal] copper ions in solution, wherein said wastewater feed contains solids sized in the range of about 0.01-1.0  $\mu\text{m}$  in an amount higher than about 100 mg/l; and

[(b)] (c) a chemical precipitation unit [operation] connected directly to said carbon bed, for receiving a carbon bed

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product stream from said carbon bed and for removing said [metal] copper ions from solution.

13. (Amended) Apparatus for removing metal ions from wastewater as set forth in Claim 12, wherein said wastewater feed contains solids in an amount higher than about 500 mg/l.

14. (Amended) Apparatus for removing metal ions from wastewater as set forth in Claim 12, wherein said wastewater feed contains hydrogen peroxide and said carbon bed product stream has concentration levels of hydrogen peroxide less than about 1 mg/l (1 ppm).

17. (Amended) Apparatus for removing metal ions from wastewater as set forth in Claim 15, wherein said chemical precipitation unit [operation] comprises organic chemical means for contacting said carbon bed product stream [metal] copper ions with an organic carbamate to precipitate said copper ions.

18. (Amended) Apparatus for removing metal ions from wastewater as set forth in Claim 15, wherein said chemical precipitation unit [operation] comprises organic chemical means

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for contacting said carbon bed product stream [metal] copper ions with dithiocarbamate to precipitate said copper ions.

19. (Amended) Apparatus for removing metal ions from wastewater as set forth in Claim 15, wherein said chemical precipitation unit [operation] comprises inorganic chemical means for contacting said carbon bed product stream [metal] copper ions with iron sulfate ( $\text{FeSO}_4$ ) or aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) to co-precipitate said copper ions.

Please add the following new Claims.

21. Apparatus for removing metal ions from wastewater, comprising:

(a) a chemical mechanical polishing unit for chemical mechanical polishing integrated circuits, said chemical mechanical polishing unit having a chemical mechanical polishing effluent discharge for discharging a wastewater stream containing hydrogen peroxide and solids sized in the range of about 0.01-1.0  $\mu\text{m}$  in an amount higher than about 500 mg/l and a byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l;

(b) a carbon bed connected directly to said chemical mechanical polishing effluent discharge, said bed providing means for receiving said wastewater stream containing said solids, hydrogen peroxide, and copper ions in solution; and

(c) a chemical precipitation unit connected directly to said carbon bed for receiving a carbon bed product stream from said carbon bed and organic chemical means for contacting said carbon bed product stream metal ions with dithiocarbamate to precipitate said copper ions for removing said copper ions from solution.

22. Apparatus for removing metal ions from wastewater, comprising:

(a) a chemical mechanical polishing unit for chemical mechanical polishing integrated circuits, said chemical mechanical polishing unit having a chemical mechanical polishing effluent discharge for discharging a wastewater stream containing hydrogen peroxide and solids sized in the range of about 0.01-1.0  $\mu\text{m}$  in an amount higher than about 500 mg/l and a byproduct polishing slurry containing copper ions at a level in the range of about 1-100 mg/l;

(b) a carbon bed connected directly to said chemical mechanical polishing effluent discharge, said bed providing means for receiving said wastewater stream containing said solids, hydrogen peroxide, and copper ions in solution; and

(c) a chemical precipitation unit connected directly to said carbon bed for receiving a carbon bed product stream from said carbon bed and inorganic chemical means for contacting said carbon bed product stream metal ions with iron sulfate ( $FeSO_4$ ) or aluminum sulfate ( $Al_2(SO_4)_3$ ) or aluminum sulfate to co-precipitate said copper ions.